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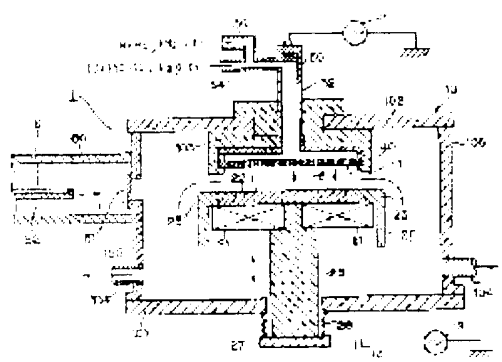
(54) PLASMA CVD SYSTEM AND FORMATION OF OXIDE FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a plasma CVD system that delivers high film quality improvement effect.
SOLUTION: Reactive gases are pumped into the reaction chamber of a plasma CVD system 1 provided with an upper electrode 20 and a lower electrode 32, and the gases are reacted with one another in a plasma atmosphere to form an oxide film on a substrate 6. Specifically, a reactive gas composed of any one of triethoxysilane, tetraethylorthosilicate or trimethoxysilane as an organic silane material, and either of nitrous oxide (N_2O) or oxygen is pumped as oxidizing agent. Further, both or either of argon (Ar) gas and ammonia (NH_3) gas or hydrazine (N_2H_4) gas is added to the reactive gas. A voltage with a frequency of 27MHz or above and 100MHz or below is applied to the upper electrode 20, and a bias voltage with a frequency of 500kHz or above and 13.56MHz or below is applied to the lower electrode 32. Thereby the ions of the additive gas(es) are accelerated and implanted in the substrate 6.



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CLAIMS

[Claim(s)]

[Claim 1] Plasma CVD equipment which is characterized by providing the following and which has a reaction chamber. The up electrode connected to the RF generator into the aforementioned reaction chamber. It has the lower electrode connected to RF bias power supply, and they are either the triethoxysilane as an organic silane material, a tetraethyl orthochromatic silicate or trimethoxysilane in the aforementioned reaction chamber. A means to feed the reactant gas which consists of either a nitrous oxide (N2O) as an oxidizer, or oxygen, and to add either to the aforementioned reactant gas further simultaneous in argon (Ar) gas, ammonia (NH3) gas, or hydrazine (N2H4) gas.

[Claim 2] It is plasma CVD equipment of the claim 1 whose power line period of RF bias power supply the power line period of a RF generator is within the limits of 27MHz or more 100MHz or less, and is within the limits of 300kHz or more 13.56MHz or less.

[Claim 3] It is plasma CVD equipment of the claim 2 whose power line period of RF bias power supply the power line period of a RF generator is 40MHz, and is 400kHz.

[Claim 4] The claim 1 which is within the limits of 10mTorr(s) - 1Torr, and is within the limits whose interval of an up electrode and a lower electrode is 20mm - 100mm equips the pressure in a reaction chamber.

[Claim 5] Equipment of the claim 1 which adds simultaneously argon (Ar) gas, ammonia (NH3) gas, or hydrazine (N2H4) gas to the aforementioned reactant gas.

[Claim 6] Equipment of the claim 1 which adds argon (Ar) gas to the aforementioned reactant gas.

[Claim 7] Equipment of the claim 1 which adds ammonia (NH3) gas to the aforementioned reactant gas.

[Claim 8] Equipment of the claim 1 which adds hydrazine (N2H4) gas to the aforementioned reactant gas.

[Claim 9] How to generate an oxide film on a substrate by feeding reactant gas in the reaction chamber of the plasma CVD equipment which has the up electrode and lower electrode which are characterized by providing the following, and making these gas react under plasma atmosphere. The triethoxysilane as an organic silane material, a tetraethyl orthochromatic silicate, or either of trimethoxysilane. Either the nitrous oxide (N2O) as an oxidizer, or oxygen.

[Claim 10] It is the method of a claim 9 that the power line period of a RF generator is within the limits of 27.0MHz or more 100MHz or less, and the power line period of RF bias power supply is 400kHz.

[Claim 11] It is the method of a claim 9 that the power line period of a RF generator is 40MHz, and the power line period of RF bias power supply is 400kHz.

[Claim 12] The pressure in a reaction chamber is the method of the claim 9 which is within the limits of 10mTorr(s) - 1Torr, and is within the limits whose interval of an up electrode and a lower electrode is 20mm - 100mm.

[Claim 13] The method of the claim 9 which feeds simultaneously argon (Ar) gas and ammonia (NH3) gas.

[Claim 14] The method of the claim 9 which feeds simultaneously argon (Ar) gas and hydrazine (N2H4) gas.

[Claim 15] The method of the claim 9 which feeds at least one kind of gas chosen from the group which consists of argon (Ar) gas, ammonia (NH3) gas, and hydrazine (N2H4) gas.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to plasma CVD equipment. Furthermore, this invention relates to the high plasma CVD equipment of the membraneous improvement effect in detail.
[0002]
[Description of the Prior Art] In manufacture of a semiconductor IC, there is a process which forms the thin film of a silicon oxide on the surface of a substrate. The chemical vapor growth (CVD) is used for the formation method of a thin film. Although there are the three methods of an atmospheric pressure method, a reduced pressure method, and the plasma method in CVD, to the VLSI as which a highly precise thin film is required for the latest high quality, it is observed noting that the plasma method is suitable.
[0003] The plasma method impresses and plasma-izes high-frequency voltage to the reactant gas injected in the vacuum, energy required for a reaction is acquired, good membraneous quality is obtained with the homogeneity of thickness, and, moreover, it excels in many respects -- film formation speed is quick.
[0004] the formation material of the silicon oxide by the plasma method -- for example, SiH4 etc. -- although used, the fall of a step coverage (level difference covering nature) has posed a problem with detailed-izing of a semiconductor device Instead of this mono-silane gas, the triethoxysilane (TRIES) [SiH (OC two H5)3] of a liquid has come to be used recently. Triethoxysilane is because the precise film excellent in the step coverage can be formed. When forming a silicon oxide using triethoxysilane, triethoxysilane is made to heat and evaporate and a reaction chamber is supplied as triethoxysilane gas.
[0005] With increase of wiring density, wiring stray capacity increases, consequently a device working speed falls. Furthermore, global flattening becomes difficult with the overhang of a formation oxide film. In recent years, the fluorine system gas (for example, CF4, C2F6, etc.) addition plasma CVD method an effect is in the high rank difference covering nature of the reduction in the dielectric constant of a multilayer interconnection and wiring is proposed. However, by the aforementioned method, Si-F combination is included in an oxide film, and moisture moisture absorption is remarkable. Consequently, Si-OH and H2O occurs and there is a problem that membraneous quality deteriorates. Moreover, water permeability is in the film itself, and moisture will be made to penetrate easily if a film with much content moisture is intervened in between. Therefore, the electrical property of devices, such as degradation of hot carrier resistance and a shift of SURESSHO hold voltage (Vth), becomes unstable with the moisture in a film. Furthermore, since the moisture incorporated in the film produces various phenomena which are made to desire and are not cut at a next sputtering process, it is not very desirable.
[0006] For this reason, the formation method of the reduction in a dielectric constant and a high moisture resistance oxide film is searched for strongly. The method of introducing a fluorine (F) as the low dielectric constant-ized method of an oxide film is mentioned the place by present. However, if fluorine system gas, such as CF4 or C2F6, is added in the triethoxysilane system of reactant gas with parallel monotonous type CVD (single cycle) equipment as aforementioned, the Si-F combination in an oxide film will be unstable, and membraneous quality will deteriorate. Si-F combination is also stabilized by the oxide film deposited in the efficient consumer response (electron cyclotron resonance) CVD system on the other hand when membranes were formed by SiF4-O2 of reactant gas, and quality membraneous quality is obtained. However, from the former, an efficient consumer response (electron cyclotron resonance) CVD system has a problem in cost, and cannot be used universally.
[0007]
[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the plasma CVD equipment which has the high membraneous improvement effect.
[0008]
[Means for Solving the Problem] The aforementioned technical problem has the up electrode connected to the RF generator, and the lower electrode connected to RF bias power supply. In the aforementioned reaction chamber, the triethoxysilane as an organic silane material, a tetraethyl orthochromatic silicate, or either of trimethoxysilane. The reactant gas which consists of either a nitrous oxide (N2O) as an oxidizer or oxygen is fed. Furthermore, it is solved by the plasma CVD equipment characterized by having a means to add either to the aforementioned reactant gas simultaneous in argon (Ar) gas, ammonia (NH3) gas, or hydrazine (N2H4) gas.
[0009] A RF generator has the 27.0MHz or more RF-generator frequency of 100MHz or less, and RF bias power supply has the 300kHz or more RF bias-power-supply frequency of 13.56MHz or less. Preferably, a RF generator has the RF-generator

frequency of 40MHz, and RF bias power supply has the RF bias-power-supply frequency of 400kHz
[0010]
[Embodiment of the Invention] Drawing 1 is the typical block diagram of the plasma CVD equipment of this invention. In drawing, a reaction chamber (chamber) 10 is made airtight, fixes the metal nozzle section 30 to the cover plate 102 of a reaction chamber 10, and supports the shower electrode 40 of the shape of a disk which has many micropores 41 which are the products made from aluminum and are penetrated from the upper surface in the lower part on the inferior surface of tongue with an insulating ring 103. Let this be the up electrode 32. RF generator 7 which impresses high-frequency voltage to the shower electrode 40 is formed. Face to face is stood against the up electrode 32, and the lower electrode 20 is arranged. The lower electrode 20 is supported by the support 25, and this support 25 is constituted possible [rise and fall], and it can change an inter-electrode interval. A sign 26 shows airtight bellows. Moreover, a sign 27 shows a support plinth. A susceptor 22 is arranged in the upper part of a support 25, the heater 21 is arranged by the lower part of a susceptor 22, and the heater covering 23 is formed in the circumference of a susceptor 22 and a heater 21. The susceptor 22 is connected to the RF bias power supply 9 which impresses RF bias voltage through a metal support 25 and a metal plinth 27. In reaction processing, the gate 51 of carrying-in taking-out way 50 established in the side 105 of a reaction chamber 10 is opened, a substrate 6 is carried in with carriage 52, and it lays in the upper surface abbreviation center section of the susceptor 22. The gate is closed, and after making the interior of a reaction chamber into a predetermined degree of vacuum by exhausting from a duct 104, a susceptor is heated at a heater, and it the substrate laid in this becomes predetermined temperature, predetermined reactant gas and/or predetermined addition gas will be fed in a reaction chamber from inlets 34 and 36. Gas is injected towards a substrate through the nozzle section 30 from the micropore 41 of a shower electrode.
[0011] In this invention, the frequency of RF generator 7 is 27.0MHz or more 100MHz or less. The frequency of the RF generator used by the up electrode of conventional plasma CVD equipment was about -13.56MHz. In such low frequency, membrane formation speed is slow under extensive inter-electrode one and a low voltage condition, and the silicon oxide film which has a property good enough is not obtained. The reason conventional plasma CVD equipment uses low frequency is easy maintenance of equipment]. Compared with microwave (2.45GHz), the reason using this frequency band is easy handling, and is because it is still comparatively [in cost] cheaper. Moreover, when it was about [-13.56MHz] frequency, there was an advantage of being able to extend or narrow plasma. However, in this invention, the power line period higher than before for whether it being ** is used. Thus, if a high power line period is used, plasma density will go up and membrane formation speed sufficient also in the high-vacuum state will be obtained. Moreover, if it will be in a high-vacuum state, since the collision of the ion itself will be lost, the ion itself can be accelerated further and it can be made to collide with a substrate. Consequently, the reforming effect on the front face of a film is fully demonstrated, and the silicon oxide film which has the outstanding membraneous quality is obtained.
[0012] If high frequency is impressed to an up electrode, although "electronic ******" will be made on an up electrode front face and ion will be concentrated around an electrode, it does not move toward a substrate. For this reason, in this invention, self-bias is applied to a substrate side by impressing RF bias-power-supply frequency to a susceptor. The ion of the up electrode circumference is pulled toward a substrate side by this self-bias, and acceleration takes place. The frequency of the RF bias power supply 9 has desirable within the limits of 300kHz - 13.56MHz. Since un-arranging -- are easy to generate the injury by plasma on the frequency of less than 300kHz, and the effect of self-bias sufficient on frequency higher than 13.56MHz is not acquired on the other hand -- arises, it is not desirable. It is desirable to form the blocking capacitor 12 between the RF bias power supply 9 and a susceptor 22. The reason for forming this blocking capacitor 12 is for forming self-bias in a lower electrode side
[0013] Drawing 2 (A) uses only a silicon alkoxide like triethoxysilane (TRIES), and shows the oxide-film configuration formed of the conventional method using the single frequency of 13.56MHz. According to the conventional method, the upper-limit periphery section of an oxide film ******s , and it becomes overhang-like. In near and detailed wiring of 0.35 micrometers or less, a void (opening) occurs [the covering configuration of the oxide film formed on wiring] in conformal (wiring side wall thickness = wiring ******) one, and global flattening becomes difficult. On the other hand, although the covering configuration of the oxide film formed on wiring shows directivity (side wall thickness < ******) by the 2 cycle method for impressing the RF of frequency different, respectively to an up electrode and a lower electrode as shown in drawing 2 (B), in a process 0.35 micrometers or less, the thickness of the side-attachment-wall section becomes extremely thin with about 100nm. Therefore, the improvement in membraneous of the side-attachment-wall section becomes indispensable. In addition, in the sign 60 in drawing, 62 shows wiring and 64 shows a silicon oxide for a substrate, respectively.
[0014] The water permeability of the plasma oxidation film formed by 2 cycle excitation CVD was evaluated. The pusher cooker (PCT) method was used for the appraisal method. An evaluation sample is the structure which deposited 200nm of PSG films on Si base, and deposited 200nm of plasma oxidation films to evaluate on it. A humidification examination is performed for this sample under the temperature of 121 degrees C, 100% of humidity, and the conditions of pressure 2atm. FT-IR measurement is performed before and after an examination, and absorbance change of P=O combination of the 1320cm-1 neighborhood is investigated. When this P=O combination decreases in connection with the passage of time, it is shown that the moisture of a plasma oxidation film is penetrating on the PSG film. The principle of this appraisal method is typically shown in drawing 3 (A). Drawing 3 (B) is the property view showing permeable evaluation of the plasma oxidation film formed by 2 cycle excitation CVD. Drawing 3 (B) shows test time to a horizontal axis, and shows the rate to which the absorbance of P=O combination decreased on the vertical axis. It turns out that the moisture resistance which was excellent, without conventional P-TEOS (single cycle method) reaching to 50% or less even if the plasma TEOS oxide film of 2 cycle excitation exceeds 200 hours about a

triethoxysilane film for 90 hours to the time when the coefficient of water permeability of the absorbance of P=O combination becomes 5 % or less being 20 hours is shown.
[0015] The relation between the reaction chamber internal pressure about the plasma stable electric discharge in a reaction chamber and an electrode spacing is shown in drawing 4. In the case of 13.56MHz conventional frequency, in order to obtain a certain amount of membrane formation speed, the ********** (5mm - 8mm) field (field shown by ** in drawing 4) has been used. However, in this invention, the former of a generation pressure is low 1-2 figures, and it performs film generation in the field (field shown by ** in drawing 4) which also extended the electrode spacing 10mm or more. On the other hand, if it discharges in the 13.56MHz single cycle conventional in this field, inter-electrode plasma density runs short, and there is a problem that electric discharge becomes unstable. Then, in this invention, in order to obtain stable electric discharge under an extensive electrode spacing and low voltage conditions, membranes are formed using a RF generator 27 moreMHz or more using 2 cycle excitation. Consequently, formation of the oxide film which was excellent in level difference covering nature with few overhangs with the increase in the amount of vertical-component ion required for the stability of the plasma electric discharge under the low voltage by improvement in plasma density and formation of a directive film was attained.
[0016] The bias output dependency over the etch rate of the plasma oxidation film formed in drawing 5 by 2 cycle excitation CVD is shown. The sample film formed membranes by the reactant gas of triethoxysilane and a nitrous oxide, and processing liquid used the fluoric acid of 1:99. It turns out that an etch rate will fall if the oxide film formed with which pressure band also impresses bias, an etch rate also falls with the increase in a bias output further, and a film makes it precise.
[0017] By making membrane formation gas mix argon gas, and impressing bias in layer insulation film formation, especially, sputtering and membrane formation advance simultaneously and a step coverage is improved.
[0018] The addition gas chosen from the group which consists of ammonia, a hydrazine, and an argon can be fed in a reaction chamber that it is together or separately with the reactant gas which consists of triethoxysilane and nitrous-oxide gas. If it feeds together with reactant gas, the above membraneous improvement effects will be acquired simultaneously with membrane formation of a plasma triethoxysilane film. Addition gas can also be used after membrane formation of a plasma triethoxysilane film because of the surface treatment of this film. The completely same membraneous improvement effect as the above is acquired also with the surface treatment after membrane formation.
[0019] As for the pressure of the reaction chamber at the time of performing membrane formation processing, it is desirable that it is within the limits of 10mTorr - 10Torr. In conventional plasma CVD equipment, if membrane formation processing is carried out by inter-electrode [30mm] by the pressure of 10mTorr(s) using the RF-generator frequency of 13.56MHz, the stable electric discharge will not be obtained but most membrane formation speed will become zero. On the other hand, by this invention, since self-bias is impressed to a lower electrode while impressing the RF-generator voltage of 27MHz ** to an up electrode, a very high membrane formation speed can be attained also by the pressure of 10mTorr. As for reaction chamber internal pressure, in this invention, it is desirable to maintain the interval of an up electrode and a lower electrode within the limits of 20mm - 100mm within the limits of 10mTorr(s) - 1Torr again.
[0020] A 40MHz RF can be impressed to an up electrode, a 400kHz RF can be impressed to a lower electrode, respectively, and membranes can be formed to the wafer supported by the lower electrode 3. 2 cycle excitation plasma CVD method according by this method to the 13.56MHz conventional plasma CVD method, 13.56MHz, and bias impression -- comparing -- high-density plasma -- it can obtain -- order -- the silicon oxide which has a taper coverage configuration can be formed on wiring In the layer insulation film formation after 64MDRAMs, it becomes difficult to embed between wiring by the void free-lancer by reduction (for example, 0.25-micrometer rule) of the space between wiring by the conventional silicon oxide / SOG film / "silicon-oxide" structure, and an improvement of the coverage configuration of a silicon oxide is needed. With the equipment of this invention, a void free-lancer's layer insulation film can be formed also in the above-mentioned structure between three layers by setting up electrode impression frequency to 40MHz which hits about 3 times over the past, and impressing 400kHz bias to a lower electrode side.
[0021]
[Effect of the Invention] According to this invention, as explained above, self-bias is formed in a substrate side, and RF bias can be impressed now from a lower electrode so that the ion in plasma may be accelerated and incidence can be carried out to a substrate. For this reason, the film property of an oxide film and membranous hygroscopicity can be made to improve by adding either to the reactant gas which consists of either [either the triethoxysilane as an organic silane material, a tetraethyl orthochromatic silicate or trimethoxysilane and] a nitrous oxide as an oxidizer, or oxygen simultaneous in argon gas, ammonia gas, or hydrazine gas, and carrying out acceleration incidence of these ion to it at a substrate.

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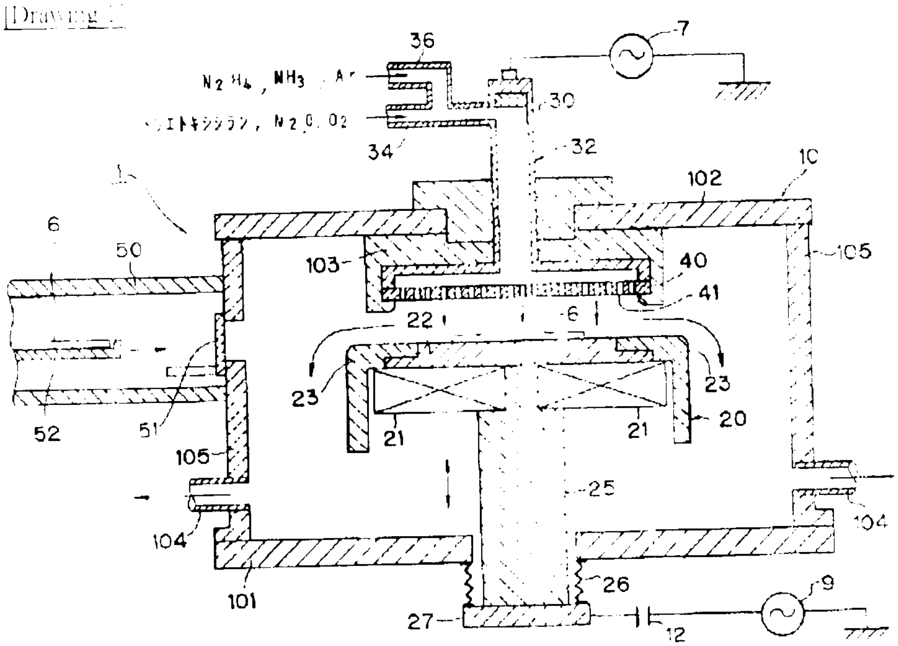
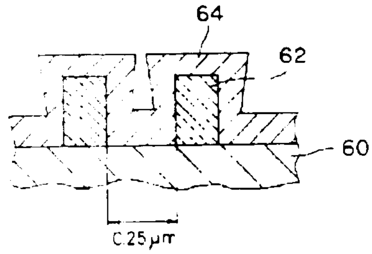
DRAWINGS

[Drawing 1]



[Drawing 2]

(A)



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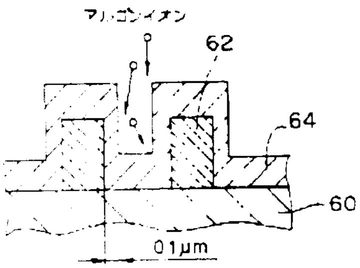
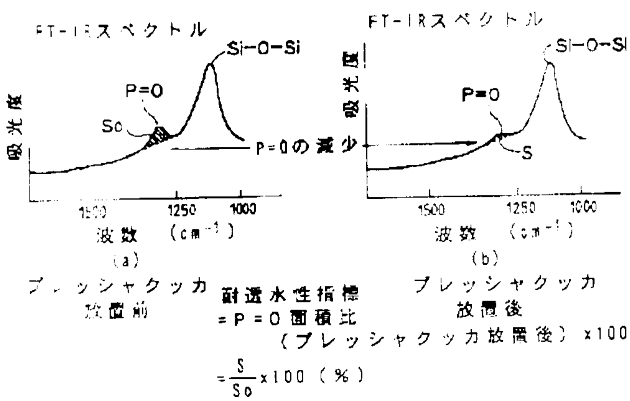


[Drawing 3]

(A)



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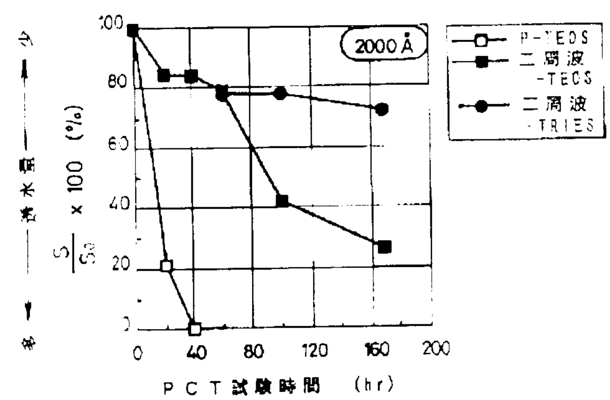
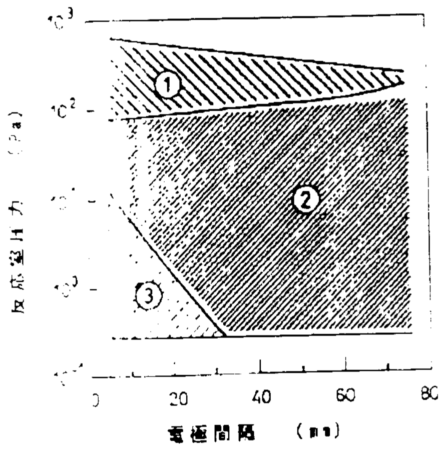


[Drawing 4]

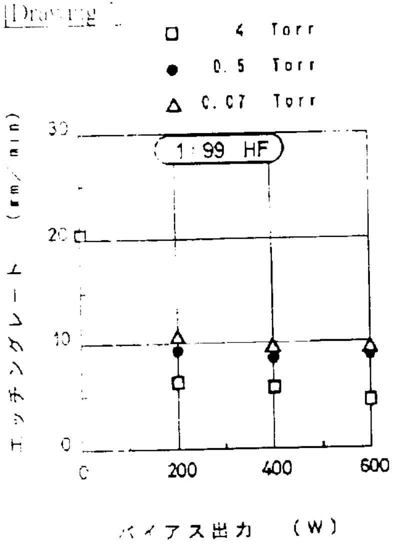


① 電極間で安定放電する領域

② 電極間及びRF印加電極周囲で安定放電する領域

③ RF電極周辺のみで放電する領域

[Drawing]



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